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REMARKS

This paper is filed in response to the final Office Action mailed on March 9, 2004. Presently, Claims 1-11 are pending. Claims 1-11 have been examined and stand rejected. Reconsideration and allowance of Claims 1-11 is respectfully requested. In the alternative, if allowance is refused, applicants respectfully request entry of the amendment for purposes of appeal.

The Rejection of Claims 1-11 Under 35 U.S.C. § 112, First Paragraph

Claims 1-11 are rejected under 35 U.S.C. § 112, first paragraph, as failing to comply with the written description requirement.

Applicants respectfully disagree. The term "non-regenerated" would be understood by persons of ordinary skill in the art to be descriptive of applicants' method. Nevertheless, Claim 1 has been amended to delete the term "non-regenerated."

Accordingly, the withdrawal of the rejection of Claims 1-11 under 35 U.S.C. § 112, first paragraph, is respectfully requested.

The Rejection of Claims 1-11 Under 35 U.S.C. § 103(a)

Claims 1-11 are rejected under 35 U.S.C. § 103(a) as being unpatentable over Gannon et al. (U.S. Patent No. 6,042,769) in view of WO 99/16960 and Samuelsson (U.S. Patent No. 5,985,097) with or without Luo et al. (U.S. Patent No. 6,210,801).

An obviousness rejection requires that there be a suggestion or motivation either in the references or in the knowledge that is generally available to modify a reference or to combine references. In addition, there must be a reasonable expectation of success and all the elements of the claims must be taught or suggested by the prior art. The motivation or suggestion cannot be taken from the applicants' disclosure.

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In relevant part, Claim 1 recites "contacting an alkaline pulp comprising cellulose and at least about 7% hemicellulose under alkaline conditions with an amount of an oxidant sufficient to reduce the average degree of polymerization of the cellulose to within the range of from about 200 to about 1100, without substantially reducing the hemicellulose content of the pulp or substantially increasing the copper number."

In direct contrast, Gannon describes a lyocell fiber treatment that reduces the lyocell fiber's degree of polymerization by about 200 units. A lyocell fiber is described in the background section of the present application as being precipitated (i.e., regenerated) from an organic solvent, such as N-methylmorpholine-N-oxide. In direct contrast, pulp is a precursor material that has not undergone dissolution and consequently is not regenerated. Differences exist between the cellulose in pulp and the cellulose in a regenerated lyocell fiber and consequently a "pulp" and a "lyocell fiber" are recognized in the art as materially different. Applicants direct the attention of the Examiner to the exhibits attached with this amendment, beginning with the E. Sjöström publication, and specifically, to page 53 describing and showing the differences of Cellulose I, which is native cellulose, compared with regenerated cellulose, Cellulose II, which is cellulose in lyocell fibers. Furthermore, on page 55, the publication states, "Cellulose II is formed whenever the lattice of Cellulose I is destroyed, for example, on swelling with strong alkali or on dissolution of cellulose." Applicants submit the Gannon reference describes the treatment of Cellulose II because the Gannon reference explicitly describes the dissolution of cellulose in a solvent followed by regeneration and treatment (Col. 1, line 65), which as the publication clearly states leads to the formation of Cellulose II. See also the publication of Sven A. Rydholm, pages 116-17, describing the differences in cellulose between native cellulose (cellulose I) and regenerated cellulose (cellulose II) in lyocell fiber.

Accordingly, it is not correct to state that Gannon et al. disclose contacting an alkaline pulp under alkaline condition with an amount of oxidant, when, in fact, what is described is contacting a lyocell fiber. As discussed above, the art recognizes that pulp and lyocell fiber are not the same material. Furthermore, the Gannon reference is silent on the amount of hemicellulose.

The WO 99/16960 reference describes a pulp, wherein the cellulose in the pulp "should preferably be treated under conditions that would maintain it in the Cellulose I phase and avoid entry into the Cellulose II phase" (page 3, lines 32-33). Accordingly, there is no suggestion or motivation to use the alkaline Kraft pulp of the WO 99/16960 reference as the fiber of the Gannon reference.

Furthermore, applicants submit that even assuming if one substitutes the pulp of the WO 99/16960 reference for the lyocell fiber of the Gannon reference, such modification would destroy the intended purpose of the Gannon reference which is to increase the fibrillation tendency of a solvent-spun fiber. The Examiner states that "[i]t would have been *prima facie* obvious from the teachings of WO 99/16960 to use alkaline Kraft pulp as the fiber of Gannon et al."

The Gannon reference describes dissolving the pulp, which is then regenerated into a lyocell fiber. If the pulp, rather than lyocell fibers, is treated, it is uncertain whether the resultant lyocell fiber would have an increased tendency to fibrillate. The proposed modification of Gannon et al. to treat the pulp rather than the fiber would render the prior art being modified unsatisfactory for its intended purpose, therefore there is no suggestion or motivation to make the proposed modification. *In re Gordon*, 733 F.2d 900, 221 U.S.P.Q. 1125 (Fed. Cir. 1984); M.P.E.P. § 2143.

Furthermore, there is no description of a pulp with at least 7% hemicellulose in either the Gannon reference or the WO 99/16960 reference, so this alone would not render the claimed invention obvious from the combination of references.

With regards to the Samuelsson reference, the Examiner states "Samuelsson et al. teaches that the catalysation of the depolymerization of cellulose and hemicellulose during peroxide bleaching can be controlled by monitoring and controlling the ratio of transition metals and Mg in the pulp (column 4, lines 10-22 and 45-47). It would have been obvious to prevent the degradation of the hemicellulose and cellulose in the cellulosic material of Gannon et al. by adding the proper amount of Mg as taught by Samuelsson et al."

This statement of the Examiner addresses the issue whether a person can modify Gannon, and not whether the teachings of the references suggest or motivate one to do so. The mere fact that references can be combined or modified does not render the resultant combination obvious unless the prior art also suggests the desirability of the combination. *In re Mills*, 916 F.2d 680 16 U.S.P.Q.2d 1430 (Fed. Cir. 1990); M.P.E.P. § 2143.01. On close examination, one comes to understand that the references teach against any modification or combination.

Samuelsson describes that magnesium compounds are widely used to suppress the depolymerization of cellulose. (Col. 1, lines 41-42). However, the Gannon reference describes a reduction in the degree of polymerization of cellulose. (Col. 2, lines 3-5.) Modifying the Gannon reference by suppressing depolymerization of cellulose by adding Mg would render the Gannon reference unsuitable for its intended purpose. The object of the Gannon reference is to decrease the degree of polymerization, i.e., to depolymerize cellulose, which is opposite to suppressing depolymerization.

Claim 1 recites that the average degree of polymerization of the cellulose is reduced. Suppressing depolymerization of cellulose, as described by the Samuelsson reference, is contrary

to reducing the degree of polymerization as claimed. Assuming the addition of Mg can suppress depolymerization, the effect would be to prevent a reduction in the degree of polymerization of cellulose. When a reference directly teaches against the process that is recited by the claims, the claims are not obvious in view thereof because neither a suggestion nor motivation exists to combine one reference with the other.

The Examiner states that, "[s]ince the copper number is directly related to the cellulose degradation, see specification, page 16, lines 8-20, it would have been obvious that preventing cellulose degradation by adding Mg to the pulp during peroxide bleaching as taught by Gannon et al., would prevent an increase in the copper number."

Applicants wish to correct what appears to be a misunderstanding on the part of the Examiner. The passage taken from applicants' specification (p. 16, lines 8-20) is in the context of degradation of the cellulose and the solvent that occurs during and after dissolution of the treated pulp to form a dope, and not during the treatment of the pulp to reduce the degree of polymerization. There is no teaching from the references to reduce the degree of polymerization of cellulose without increasing the copper number at the time of reducing the degree of polymerization. Furthermore, the Examiner's reliance on applicant's own disclosure that provides the suggestion or motivation to find Claim 1 obvious, is not appropriate.

With regards to the Luo reference, the Examiner states that "[i]f necessary, it would have been obvious to prevent an increase in the copper number by treating the lyocell with sodium borohydride to decrease the copper number as taught by Luo et al."

Claim 1 recites preventing an increase in copper number during the treatment to reduce the degree of polymerization.

In direct contrast, the Luo et al. reference describes separate steps. One step for reducing the degree of polymerization of cellulose, which is followed by a second, post treatment step to

reduce the copper number, which becomes necessary because the degree of polymerization reduction step described in the Luo et al. reference causes an increase in copper number. The Luo reference therefore has to employ a post degree of polymerization reduction step to lower the copper number. (Col. 13, lines 31-39). Accordingly, the Luo et al. reference does not describe a step to "reduce the average degree of polymerization . . . without . . . substantially increasing the copper number," as recited by Claim 1.

Accordingly, none of the references describe or remotely teach or suggest the invention that is defined by Claim 1, either alone or in combination. Accordingly, withdrawal of the rejection of Claims 1-11 is respectfully requested.

The Rejection of Claims 1-11 Under 35 U.S.C. § 112, Second Paragraph

Claims 1-11 are rejected under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point and distinct claim the subject matter which applicant regards as the invention.

The Examiner states that "the term 'without substantial increasing of the copper number' when read in view of the specification includes increases up to 100%. A doubling of the copper number is a substantial increase in copper number. Thus, the term is indefinite.

The argument that a 100% increase is not a substantial increase is not convincing. A 10% increase would be a substantial increase, a 100% increase is an extremely large increase and would not be considered 'without substantial increase'."

Applicants respectfully disagree. The meaning of the phrase "without substantially increasing the copper number" is clearly apparent from the specification. "When the specification states the meaning that a term in the claim is intended to have, the claim is examined using that meaning, in order to achieve a complete exploration of the applicant's

invention and its relation to the prior art." M.P.E.P. § 2173.05(a); *In re Zeltz*, 893 F.2d 319, 13 U.S.P.Q.2d 1320 (Fed. Cir. 1989).

The term "substantially" is often used in conjunction with another term to describe a particular characteristic of the claimed invention. It is a broad term. *In re Nehrenberg*, 280 F.2d 161, 126 U.S.P.Q. 383 (C.C.P.A. 1960). The court in *In re Mattison* held that the limitation "to substantially increase the efficiency of the compound as a copper extractant" was definite in view of the general guidelines contained in the specification. *In re Mattison*, 509 F.2d 563, 184 U.S.P.Q. 484 (C.C.P.A. 1975). The court in *Andrew Corp. v. Gabriel Electronics* held that the limitation "which produces substantially equal E and H plane illumination patterns" was definite because one of ordinary skill in the art would know what was meant by "substantially equal." *Andrew Corp. v. Gabriel Electronics*, 847 F.2d 819, 6 U.S.P.Q.2d 2010 (Fed. Cir. 1988). M.P.E.P. § 2173.05(b).

As the above cases point out, the term "substantially" is not indefinite when viewed with respect to the specification or when one of ordinary skill in the art would understand what was meant by the phrase. In the present application, applicants have defined, "without substantially increasing the copper number," to be without increasing the copper number by more than about 100%, preferably not more than about 50% and most preferably not more than about 25% during the D.P. reduction step. Please see the present specification on page 16, lines 8-11. Accordingly, one of ordinary skill would readily understand what is meant by "without substantially increasing the copper number" by merely referring to the specification.

Accordingly, the withdrawal of the rejection of Claims 1-11 under 35 U.S.C. § 112, second paragraph is respectfully requested.

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CONCLUSION

In view of the foregoing amendments and remarks, applicants submit that Claims 1-11 are allowable. Accordingly, a Notice of Allowance is respectfully requested. In the alternative, applicants request entry of the amendment for purposes of appeal. If the Examiner has any further questions or comments, the Examiner may contact the applicants' attorney at the number provided below.

Respectfully submitted,

CHRISTENSEN O'CONNOR
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Pulping Processes

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Pioneer of modern pulping chemistry

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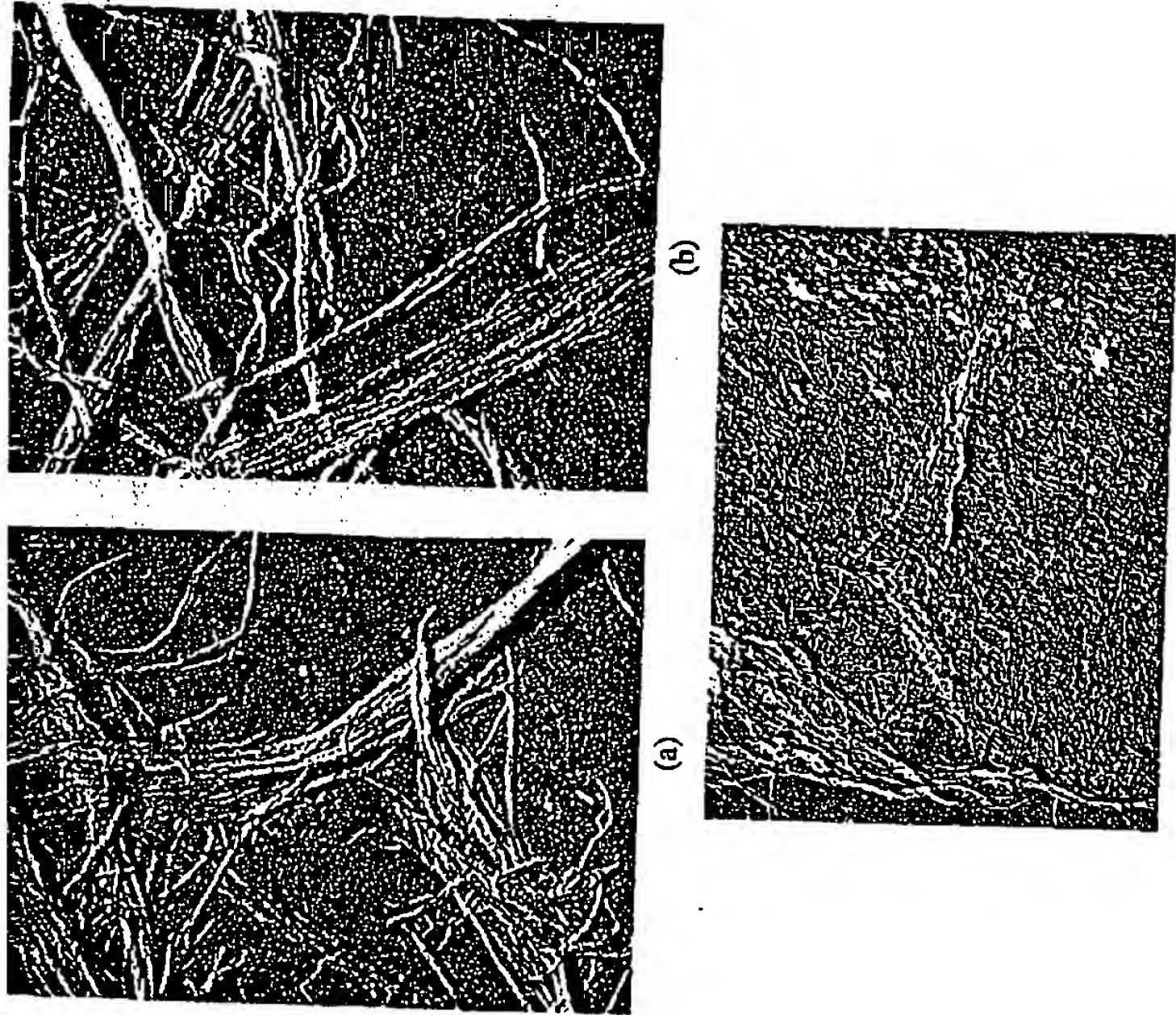


Fig. 4.6. Electron micrographs of cellulose microfibrils and elementary fibrils, from (a) purified sprucewood pulp and (b) cotton, disintegrated by ultrasonic irradiation of the fibers in water suspension ($\times 27,000$) (Rånby) (c) As occurring in the primary wall of eucalypt fibers ($\times 9,000$) (Wardrop)

other to an extent which permits an evaluation of how far these fibrils constitute structural entities, Figure 4.6 (635). Although the values of the average width of the elementary fibrils have tended to decrease with improved resolution of the electron microscope, it is now fairly well established, that they are about 100 Å wide, 30 Å thick and of infinite length. The elementary fibrils of wood cellulose may be less wide than those of cotton, whereas animal and algal cellulose elementary fibrils may be a little wider, possibly accounting for the differences noted in the corresponding x-ray diagrams. These structural units are often intimately aggregated to microfibrils about 200–250 Å wide by means of hydrogen bonding between the respective surface layers, Figure 4.7 (235). On hydrolysis, the elementary fibrils first tend to aggregate still further (812) and then eventually disintegrate into short fragments, *micelles*, of the

same width as the elementary fibrils (370, 555, 545), Figure 4.6 (370). The average length of these fragments depends on the pretreatment, those pulps which have been alkali-treated yielding shorter micelles on hydrolysis than those which have not (414). In the former case, the micelles are about 500–1,000 Å long, corresponding to the length of molecules of DP 100–200, which is also the average DP of the hydrolyzed pulp (70). Thus the hydrolysis of cellulose suspensions is pronouncedly heterogeneous, and it is assumed that the amorphous regions form the starting points of this

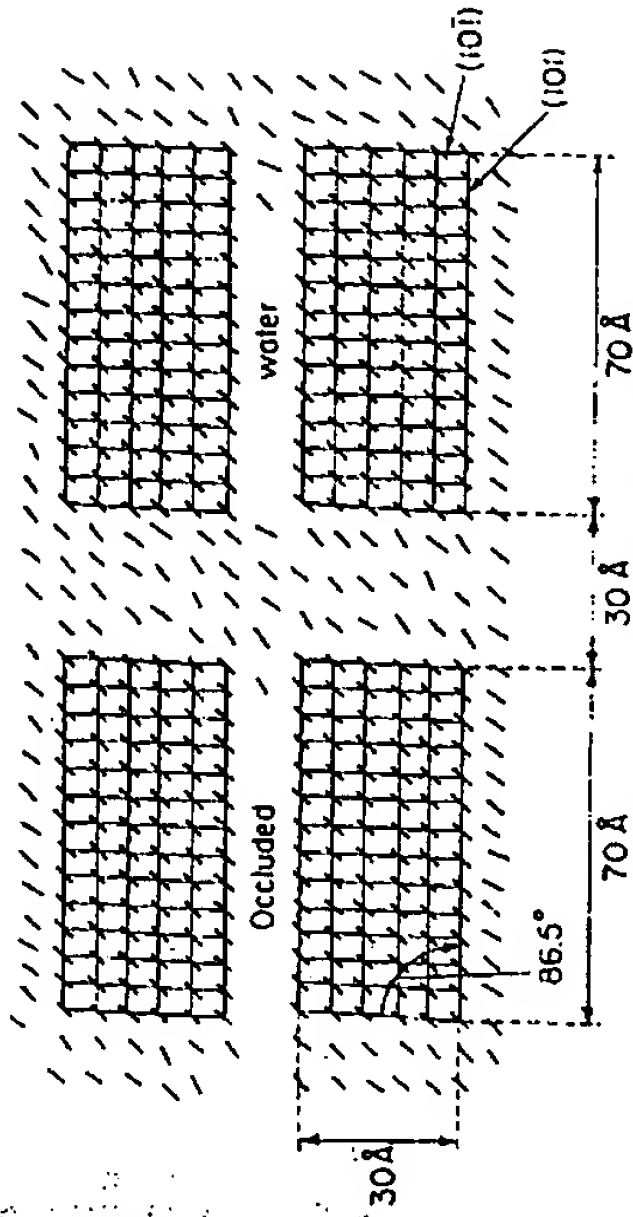


Fig. 4.7. Diagrammatic representation of a cross-section of a microfibril as an aggregation of elementary fibrils (Frey-Wyssling)

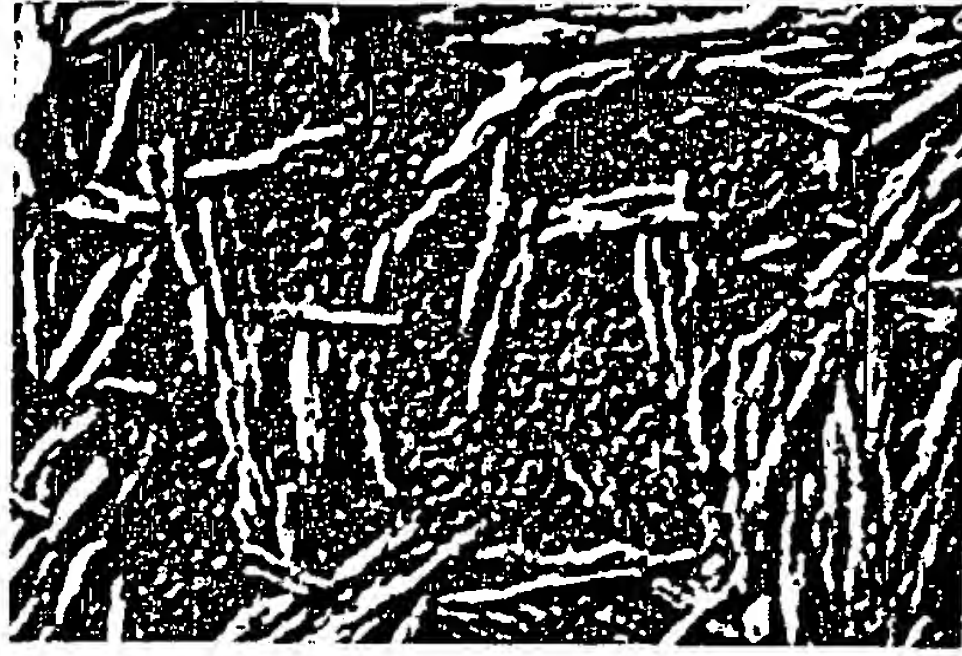


Fig. 4.8. Micelles from hydrolyzed ramie cellulose, deposited on a glass surface ($\times 47,000$) (Morehead)

attack. The degradation of the more crystalline regions first occurs in the vicinity of the amorphous regions. After the initial phase of the hydrolysis, which removes the amorphous matter and degrades the crystalline portion to a more or less constant level of DP 100–200, a second phase follows, in

fast for wood cellulose as for cotton. During that phase, the micellar length and DP of the residue from the latter material remains almost constant, whereas that from wood cellulose gradually decreases in micellar length and DP (559, 582). This indicates a higher degree of crystalline perfection in the cotton cellulose micelles (378, cf. 719). Not only alkali treatment but also drying of the original cellulose induces changes in the course of subsequent hydrolytic degradation and results in a lower DP level (378, 502), thus reflecting changes in the super-structure of cellulose. Mechanical influence, such as crushing or bending of the fibers, which is known to introduce slip planes and irregularities in the association of the elementary fibrils to larger structures, cf. Chapter 3, may cause similar disturbance within the fibrils and lead to phenomena of the same type as those previously mentioned for alkaline swelling or drying.

The detailed arrangement of the crystalline regions has been deduced from x-ray data (34, 265, 325, 550, 629, 739). An elementary cell with a rhombic symmetry was originally proposed (629), later modified (550) to a monoclinic cell with the dimensions:

$$\begin{aligned} a &= 8.3 \text{ \AA} \\ b &= 10.3 \text{ \AA} \\ c &= 7.9 \text{ \AA} \\ \beta &= 84^\circ \end{aligned}$$

as illustrated in Figure 4.9 (550). The cellulose chains are arranged parallel to the b axis and have the symmetry of a digonal screw axis (a modification suggests a distortion of every second monomer (83, 590)). The chains are parallel to each other and are considered to hold together in the a - b plane

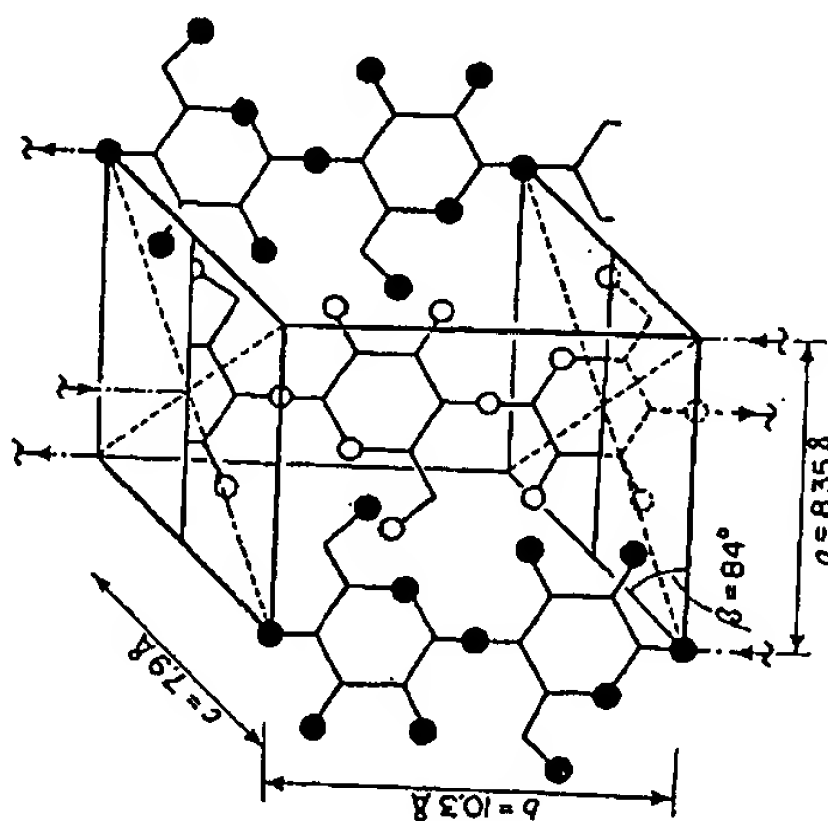


Fig. 4.9. The monoclinic elementary cell of cellulose (Meyer-Misch)

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by nitrogen bonding (a modification suggests hydrogen bonding between the *a-b* planes in the 101 direction (234)). The chains of adjacent *a-b* planes run in opposite directions and are staggered as to their vertical arrangement by the length of half a monomer. Figures 4.10-12 show the

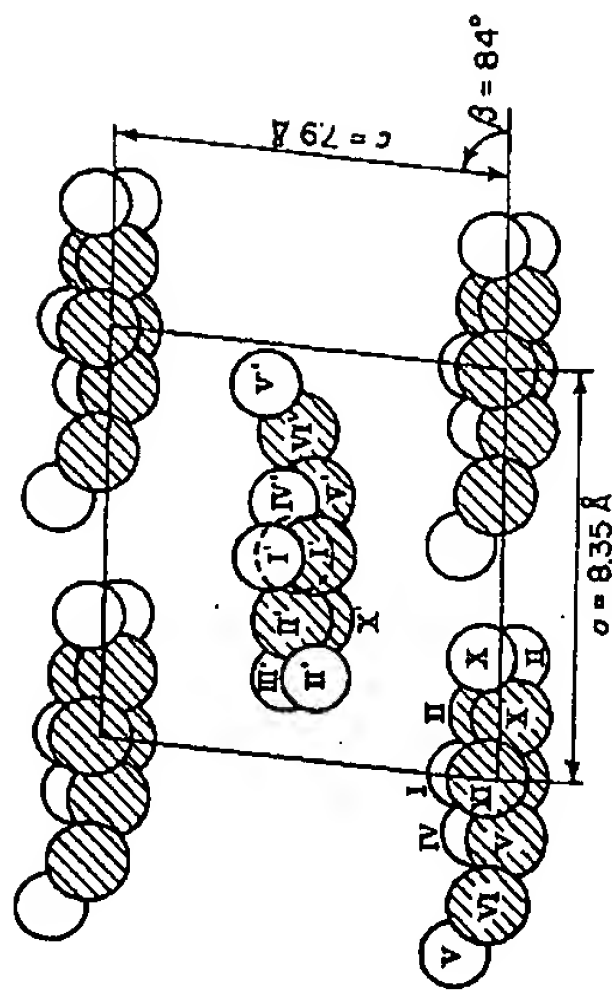


Fig. 4.10. Projection of the elementary cell of cellulose on the a - c plane perpendicular to the b -axis (Wise-Jahn)

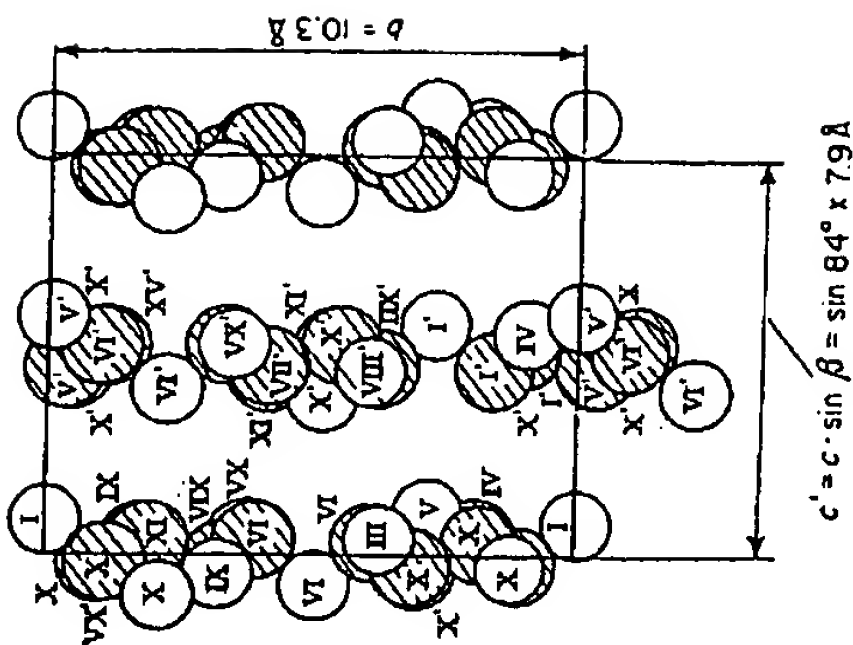


Fig. 4.1.1. Projection of the elementary cell of cellulose on the *b*-*c* plane perpendicular to the *a*-axis (Wise-Jahn)

detailed arrangement of the atoms of the elementary cell in the three projections. The hydroxyl oxygen of two adjacent chains are at a distance of only 2.5 Å in the direction of the a axis, allowing complete hydrogen bonding. The closest distance between the atoms belonging to different a - b planes is about 3.1 Å (cf. however (234)), allowing only weaker forces, i.e. the attraction of the OH-dipoles and the permanent electric moment

pounds (cuam or cuen solutions) or unstable substitution compounds, predominantly cellulose xanthate. Its x-ray diffraction diagram is shown in Figure 4.13 (635) in comparison to that of cellulose I. The x-ray studies have revealed (34, 114, 550) that cellulose II has a monoclinic elementary cell of the dimensions:

$$\begin{aligned} a &= 8.1 \text{ \AA} \\ b &= 10.3 \text{ \AA} \\ c &= 9.1 \text{ \AA} \\ \beta &= 62^\circ \end{aligned}$$

which contains four glucose monomers as in the case of cellulose I. The spatial arrangement of the chains is shown in Figure 4.14 in comparison with cellulose I. It is seen that the transformation involves a slight dis-

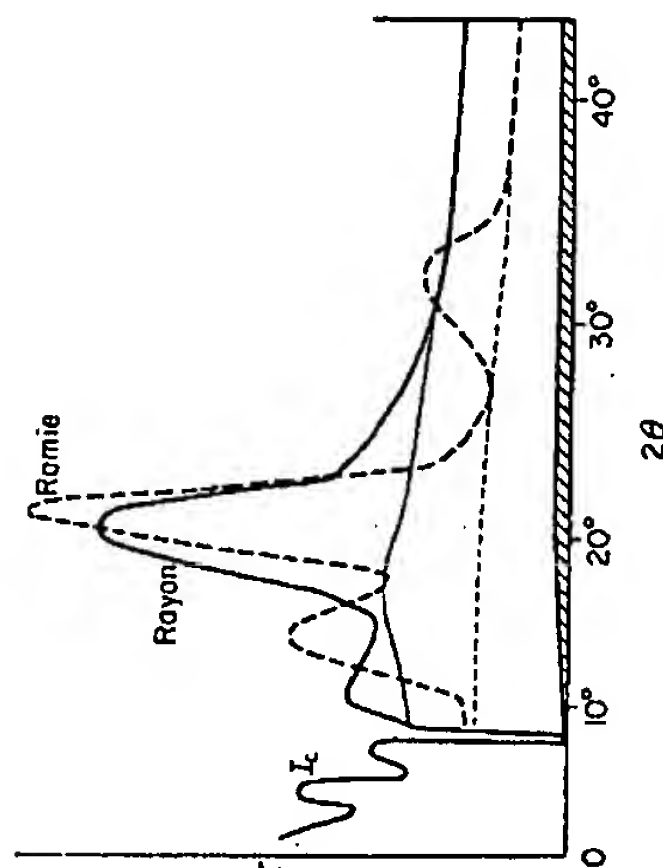


Fig. 4.13. X-ray scattering diagrams from cellulose I (ramie) and cellulose II (rayon). I_c is a reflection from a standard sample (Hermans)

tortion of the chains out of the a - b plane to form new hydrogen bonds in the $10\bar{1}$ direction. It is thereby noticed that the chains thus interconnected run in an opposite direction to the situation in cellulose I. Cellulose II seems to be the thermodynamically more stable form. On heating cellulose II to high temperatures in glycerol or alkali, it is converted to a new crystalline form which closely resembles cellulose I (68, 139, 326, 459, 551), but is probably a separate type, called high-temperature cellulose or cellulose IV (327, 372, 416), with an orthorhombic symmetry and the approximate dimensions:

$$\begin{aligned} a &= 8.1 \text{ \AA} \\ b &= 10.3 \text{ \AA} \\ c &= 7.9 \text{ \AA} \\ \beta &= 90^\circ \end{aligned}$$

indicating a denser packing than both cellulose I and II (corresponding to a density of 1.62 as compared to 1.59 for cellulose I and II and about 1.50

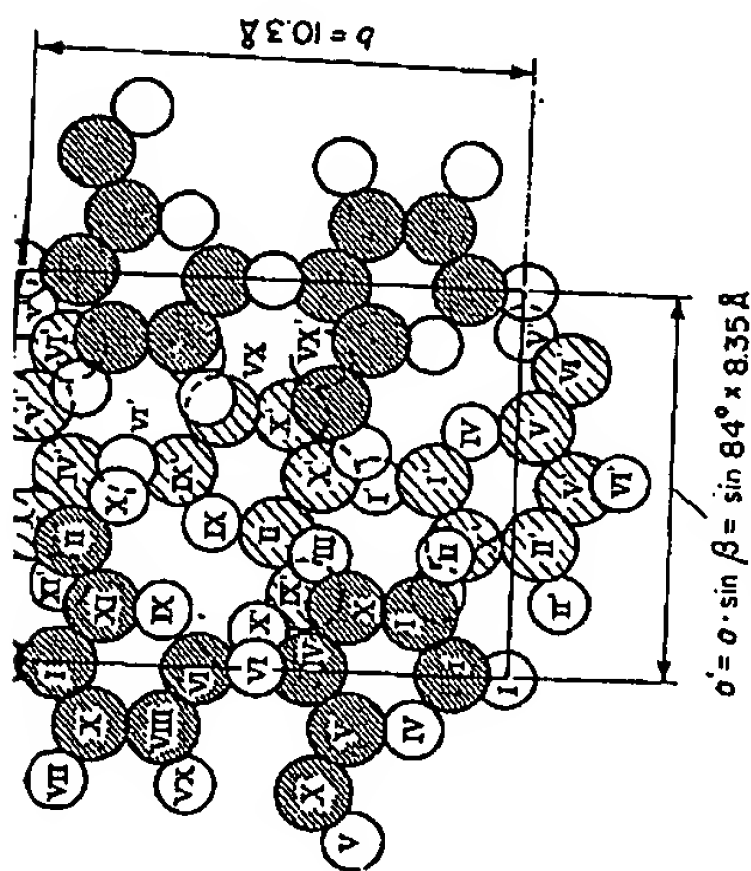


Fig. 4.12. Projection of the elementary cell of cellulose on the a - b plane perpendicular to the c -axis (Wise-Jahn)

of the C-O-C groups. The strongest forces, of covalent bonds, operate in the direction of the b axis. Recent work (83, 590, 618) indicates, that the glucose units have the $C1$ conformation (chair form) and every second unit slightly twisted (20 - 30°). Infrared analysis further suggests, that all hydroxyls are engaged in hydrogen bonding, and that an *intrachain* hydrogen bond is present between the 3-hydroxyl and the ring oxygen of the adjacent monomer (488, 524, 797). If that bond prevails also after mercerization, it would probably decrease the reactivity of the 3-hydroxyl in substitution reactions (143), cf. the subsequent section. These recent observations cause only relatively small adjustments of the classical model. A more radically new concept has also been advanced for discussion (787). Work on other polymers, such as polyethylene, nylon, etc., has indicated that chain *folding* can occur to give crystals of uniform thickness (197, 430), and it was suggested (787) that similar folding of cellulose chain molecules in the $10\bar{1}$ plane occurs, giving discontinuities for every 500 Å. The comparative rigidity of the cellulose molecules in solution (e.g. 319) is an argument against such a super-structure, but investigations on steric models indicate a U-turn diameter of only about 10 Å (644), and cellulose derivatives and even cellulose have been obtained from very dilute solutions in the form of regular, compact, lamellar crystals of microscopic size, similar to the single crystals of linear synthetic polymers mentioned above (644).

The crystalline structure described is valid for native cellulose. There are several polymorphous forms, of which that of *regenerated cellulose* is the most important. This form is also designed *cellulose II*, in contrast to *cellulose I*, native cellulose. Cellulose II is formed upon regeneration of cellulose from its solid addition compounds, such as the acid, water or alkali celluloses (cf. below), as well as from solutions of addition com-

normally used in pulping processes and is therefore of little importance, as is cellulose III, observed to form on the decomposition of ammonia cellulose (326).

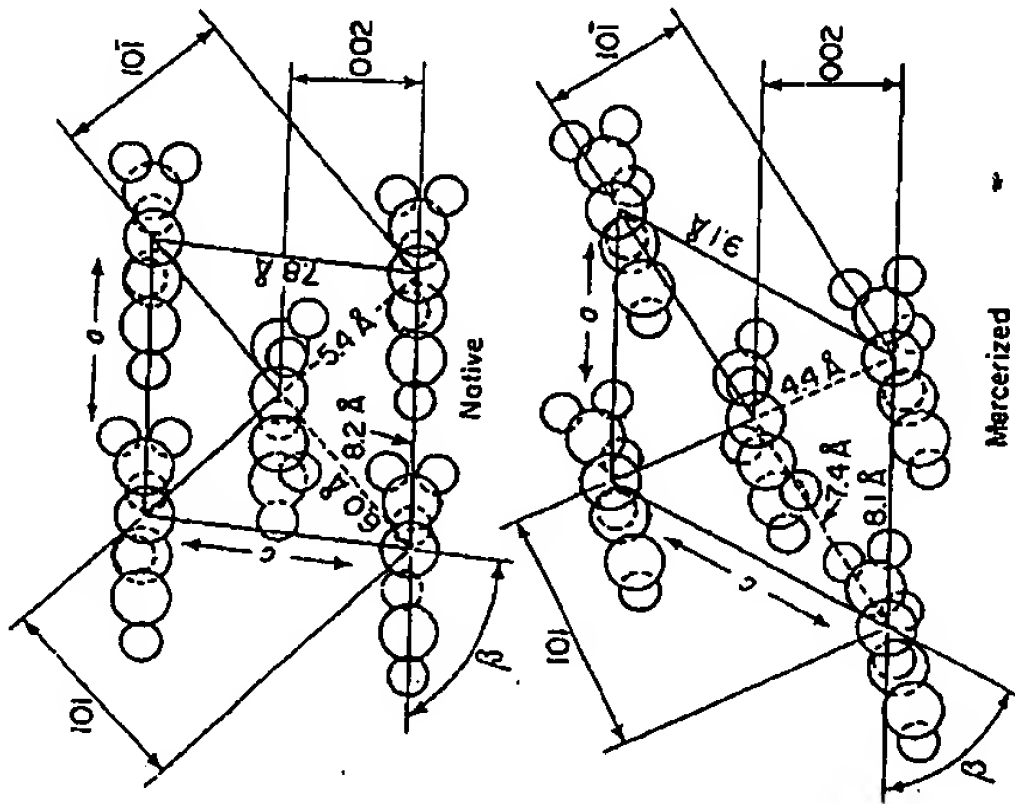


Fig. 4.14. Cross-sections of the unit cells of cellulose I and II lattices, cut at right angles to the *b*-axis, i.e. at right angles to the cellulose chains

The importance of the super-molecular structure of cellulose for its properties and its heterogeneous reactions is obvious. Only a limited fraction of its hydroxyl groups is available for interaction with water, and cellulose hence remains insoluble in water in spite of its polarity. Likewise most of its hydroxyl and acetal groups are comparatively inaccessible to chemical reagents unless the super-structure is influenced by treatment with strong swelling agents. The physical properties are influenced not only by the average molecular length and the length distribution, but also by the degree of crystallinity.

4. REACTIVITY

As just indicated, the influence of the super-molecular structure on the reactivity of cellulose is profound and has to be considered in all cellulose reactions of heterogeneous type. However, obviously the various possibilities of cellulose reactions are determined by its molecular constitution. Like all carbohydrates, the cellulose molecule is capable of reactions at its hydroxyl and acetal groups, as well as at the aldehydic end groups. The

reactions now described for cellulose will be principally possible also for the hemicelluloses, and in the section on hemicelluloses therefore only those deviations will be pointed out which result from the different carbohydrate structure of those compounds.

The hydroxyl groups react with *addition*, *substitution* and *oxidation* agents and the acetal groups undergo *hydrolysis* in acid as well as in alkaline medium. The aldehydic end groups can be *reduced* to alcohol groups, *oxidized* to carboxyl groups or *rearranged* under the influence of alkali to form either alcohol or carboxyl end groups. Since the redox and rearrangement reactions all influence the ease of hydrolysis of the glucosidic bonds, they will be treated together with hydrolysis under the heading of chemical *degradation reactions*. This category of reactions include those of importance for the pulping processes, whereas the addition and substitution reactions are of interest mainly in connection with the use of dissolving pulps. A special variant of the substitution reactions, called *grafting*, involves the incorporation of copolymers, e.g. of the polyvinyl type, usually by reacting cellulose with the monomer in a redox system, such as ceric ions (379, 710a). A radical mechanism is involved. One addition reaction, that of carbohydrates and water, is of predominant importance in the use of paper pulps. To facilitate the understanding of the various reactions, the analogous reactions with low-molecular compounds will first be treated, followed by a discussion of the reaction of cellulose in homogeneous solution, and finally the corresponding reaction in the heterogeneous two-phase system will be described.

A. Degradation reactions

(a) *Degradation of low-molecular model compounds.* Hydrolysis of glycosidic bonds occurs in both acid and alkaline medium, although much faster at low pH. The rate of reaction also varies with the type of sugar and aglycone. Table 4.18 (161, 831) gives the relative rates of hydrolysis of various methyl glycopyranosides, showing the relative stability of glucosides in acid medium and of mannosides in alkaline medium. Glycofuranosides are much more easily hydrolyzed in acid medium than

Table 4.18. Relative rates of hydrolysis of various methyl glycopyranosides (161, 831)

| | Acid hydrolysis | Alkaline hydrolysis |
|-------------------------------|-----------------|---------------------|
| Methyl- α -glucoside | 1.0 | 1.0 |
| Methyl- β -glucoside | 1.9 | 10.0 |
| Methyl- α -mannoside | 2.4 | 11.0 |
| Methyl- β -mannoside | 5.7 | 4.4 |
| Methyl- α -galactoside | 5.2 | 3.9 |
| Methyl- β -galactoside | 9.3 | 23.0 |
| Methyl- α -xyloside | 4.5 | 4.8 |
| Methyl- β -xyloside | 9.0 | 23.0 |

WOOD CHEMISTRY

Fundamentals and Applications

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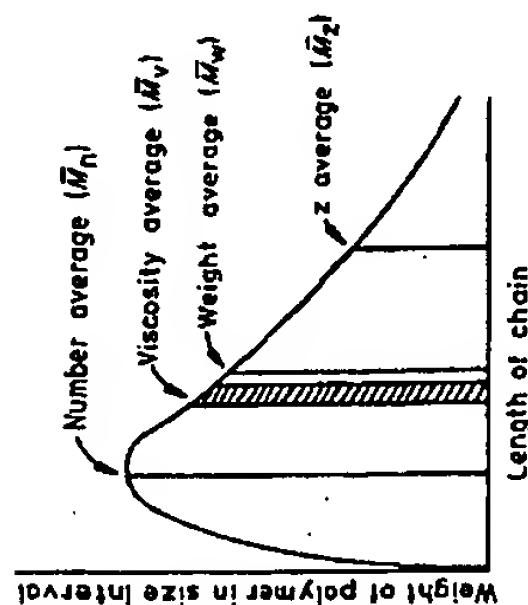


Fig. 3-10. The molecular weight distribution and the average molecular weights of a typical polymer (Billmeyer, 1965).

isolation of cellulose from wood involves risk for some degradation resulting in a reduced molecular weight.

The distribution of molecular weights can be presented statistically as illustrated by Fig. 3-10 where the weight of polymer of a given size is plotted against the chain length. The experimental measurements give an average value of the molecular weight and some methods also a molecular weight distribution. For any polydisperse system, these average values differ from each other depending on the method used. The number average molecular weight \bar{M}_n can be measured using osmometry or by determining the number of reducing end groups. The weight average molecular weight \bar{M}_w can be deduced from light scattering data. Sedimentation equilibrium data attainable by ultracentrifugation technique give so-called \bar{M}_z values. Finally, \bar{M}_v refers to the molecular weight calculated on the basis of viscosity measurements. For cellulose, the relationship between molecular weight and degree of polymerization (DP) is $DP = M/162$, where 162 is the molecular weight of anhydroglucose unit. The ratio \bar{M}_w/\bar{M}_n is a measure of polydispersity corresponding to the width of the molecular weight distribution and ranges for typical polymers from 1.5-2.0 to 20-50.

Molecular weight measurements have shown that cotton cellulose in its native state consists of about 15,000 and wood cellulose of about 10,000 glucose residues. Some polydispersity data on cellulose derivatives and polysaccharides are shown in Table 3-1. There are indications that the native cellulose present in the secondary cell wall of plants is monodisperse, that is, contains only molecules of one size. In such a case, number and weight average molecular weights ought to be identical. The cellulose in the primary cell wall, on the other hand, which has a lower average molecular

*The SI system (Système International d'Unités) recommends the term *relative molecular mass* instead of molecular weight, but because the SI term is not yet universally adopted in the polymer chemistry the latter term is used throughout this book.

TABLE 3-1. Polydispersity Values (\bar{M}_w/\bar{M}_n) of Different Polysaccharides^a

| Macromolecule | Source | $\bar{M}_w \times 10^{-5}$ | \bar{M}_w/\bar{M}_n |
|------------------------|--------------|----------------------------|-----------------------|
| Cellulose nitrate | Birch | 27 ^b | 1.9 ^c |
| Cellulose nitrate | Ramie | 24 ^b | 1.7 ^c |
| Amylose | Potato | 8.8 ^d | 1.9 ^d |
| Xylan | Birch | 0.8 ^b | 2.3 ^e |
| Xylan | Elm | 0.7 ^b | 2.4 ^e |
| Amylopectin | Waxy corn | 1700 ^b | 116 ^f |
| Hydrolyzed amylopectin | Waxy corn | 15 ^b | 25 ^f |
| Glycogen | Sweet corn | 190 ^b | 15 ^f |
| Hydrolyzed glycogen | Sweet corn | 20 ^b | 6.3 ^f |
| Glycogen | Rabbit liver | 390 ^b | 6.6 ^g |

^a From Goring (1962).

^b \bar{M}_w by light scattering.

^c \bar{M}_n by viscometry from $[\eta] = 0.0091$ DP.

^d Calculated from fractionation data.

^e \bar{M}_n by osmometry.

^f \bar{M}_n from the alkali number.

^g \bar{M}_w from sedimentation and diffusion used instead of \bar{M}_n ; usually $\bar{M}_w > \bar{M}_n$.

weight, is evidently polydisperse, being similar in this respect to the hemicelluloses.

3.2.3 The Configuration of Cellulose Molecules

Based on properties in solution such as intrinsic viscosity and sedimentation and diffusion rates, conclusions can be drawn concerning the polymer configuration. Like most of the synthetic polymers, such as polystyrene, cellulose in solution belongs to a group of linear, randomly coiling polymers. This means that the molecules have no preferred structure in solution in contrast to amylose and some protein molecules which can adopt helical conformations. Cellulose differs distinctly from synthetic polymers and from lignin in some of its polymer properties. Typical of its solutions are the comparatively high viscosities and low sedimentation and diffusion coefficients (Tables 3-2 and 3-3).

Any linear polymer molecule, even a reasonably stiff rod, will coil randomly, provided the chain is sufficiently long. In addition to the size of the monomer units, the tendency for coiling is affected by the forces between the units as well as the interaction between the polymer and the solvent. One measure of the stiffness of a polymer molecule is the end-to-end distance (R). For a polydisperse polymer the root-mean-square average of R (\bar{R}^2)^{1/2} is used. R is affected by the properties of the polymer itself as well as by the interaction of the solvent. The better the solvent the more the polymer

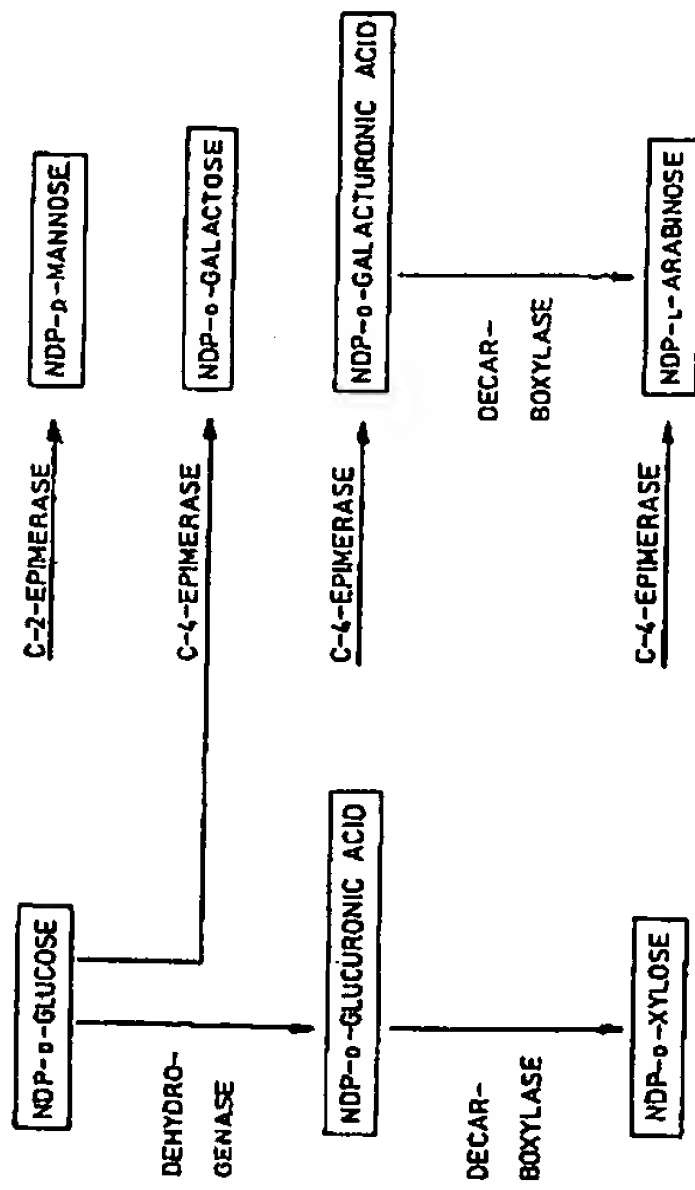


Fig. 3-4. Simplified representation of the formation of hemicellulose precursors from UDP-D-glucose or GDP-D-glucose. Note that NDP (nucleotide diphosphate) means either UDP or GDP.

3.2.1 Molecular Structure

Although the chemical structure of cellulose is understood in detail, its supermolecular state, including its crystalline and fibrillar structure is still open to debate. Examples of incompletely solved problem areas are the exact molecular weight and polydispersity of native cellulose and the dimensions of the microfibrils.

Cellulose is a homopolysaccharide composed of β -D-glucopyranose units which are linked together by (1 \rightarrow 4)-glycosidic bonds (Fig. 3-5). Cellulose molecules are completely linear and have a strong tendency to form intra- and intermolecular hydrogen bonds. Bundles of cellulose molecules are thus aggregated together in the form of microfibrils, in which highly ordered (crystalline) regions alternate with less ordered (amorphous) regions. Microfibrils build up fibrils and finally cellulose fibers. As a consequence of its fibrous structure and strong hydrogen bonds cellulose has a high tensile strength and is insoluble in most solvents. The physical and chemical behavior of cellulose differs completely from that of starch, which clearly demonstrates the unique influence of stereochemical characteristics. Like cellulose, the amylose component of starch consists of (1 \rightarrow 4)-linked D-glucopyranose units, but in starch these units are α -anomers. Amylose



Fig. 3-5. Structure of cellulose. Note that the β -D-glucopyranose chain units are in chair conformation (4C_1) and the substituents HO-2, HO-3, and CH₂OH are oriented equatorially.

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occurs as a helix in its solid state and sometimes also in solution. Amylopectin, the other starch component, is also a (1 \rightarrow 4)- α -glucan but is highly branched. The branched structure accounts for its extensive solubility, since no aggregation can take place.

The crystalline structure of cellulose has been characterized by X-ray diffraction analysis and by methods based on the absorption of polarized infrared radiation. The unit cell of native cellulose (cellulose I) consists of four glucose residues (Figs. 3-6 and 3-7). In the chain direction (c), the repeating unit is a cellobiose residue (1.03 nm), and every glucose residue is accordingly displaced 180° with respect to its neighbors, giving cellulose a 2-fold axis. It has now been established and largely accepted that all chains in native cellulose microfibrils are oriented in the same direction, that is, they are parallel (Fig. 3-7). There are two hydrogen bonds within each cellulose chain, namely from O(6) in one glucose residue to O(2)H in the adjacent glucose and also from O(3)H to the ring oxygen, as shown in Fig. 3-8. The chains form a layer in the a-c crystallographic plane, where they are held together by hydrogen bonds from O(3) in one chain to O(6)H in the other. There are no hydrogen bonds in cellulose I between these layers, only weak van der Waal's forces in the direction of the b-axis. Native cellulose therefore has a chain lattice and a layer lattice at the same time.

Regenerated cellulose (cellulose II) (Fig. 3-6) has antiparallel chains (Fig. 3-9). The hydrogen bonds within the chains and between the chains in the

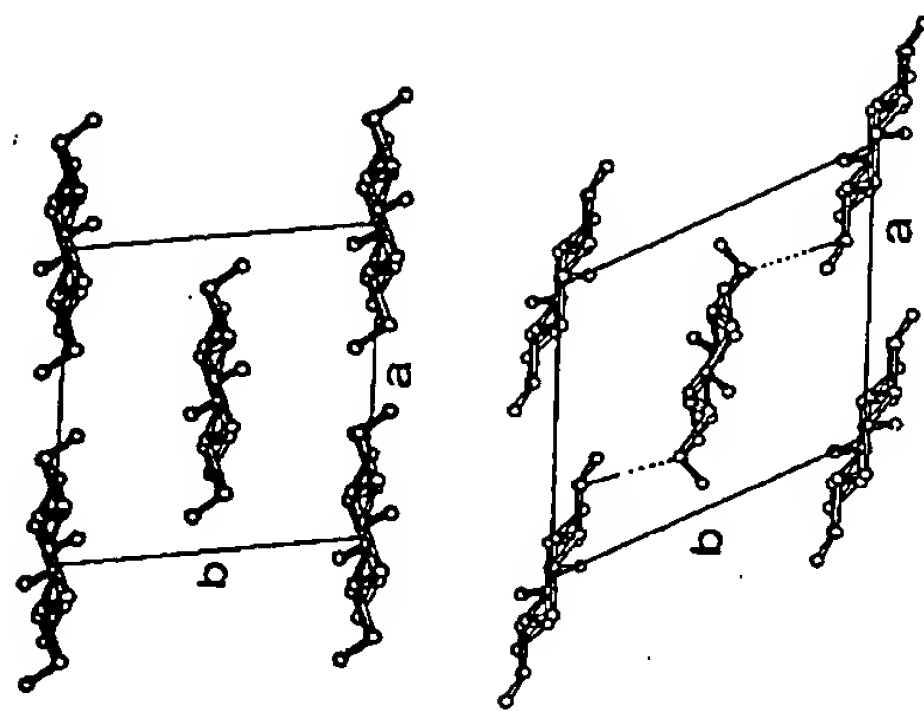


Fig. 3-6. Axial projections of the structures of native cellulose (cellulose I, above) and regenerated cellulose (cellulose II, below). (Reproduced from Kolpak et al., 1978, *Polymer* 19, 123-131, by permission of the publishers, IPC Business Press Ltd. ©.)

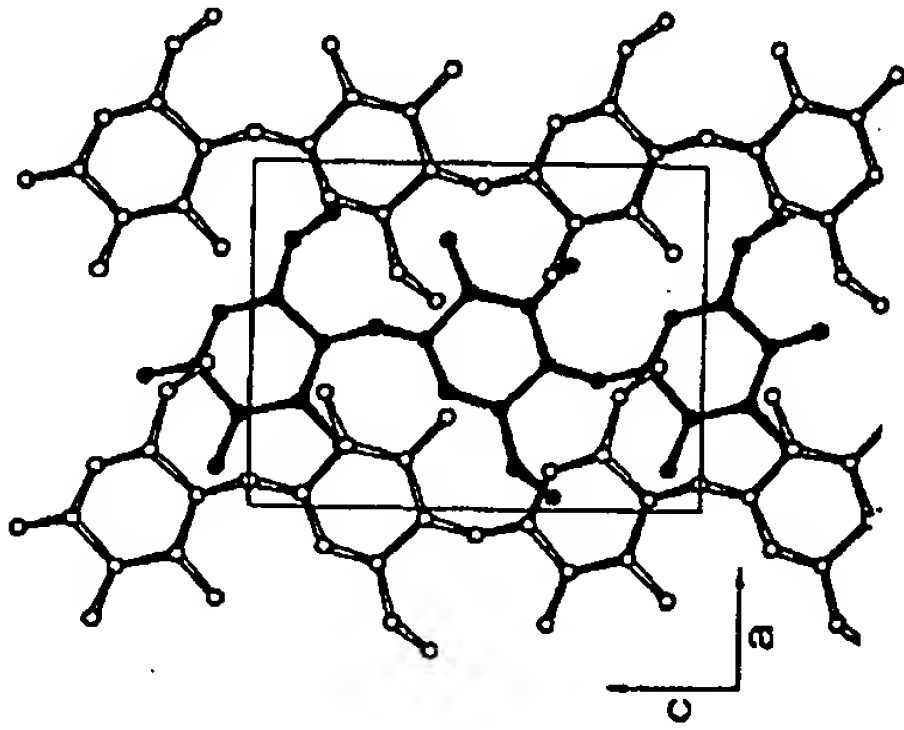


Fig. 3-7. Projection of the chains in cellulose I perpendicular to the *ac* plane. The center chain (black) is staggered but is parallel with the two corner chains (Gardner and Blackwell, 1974).

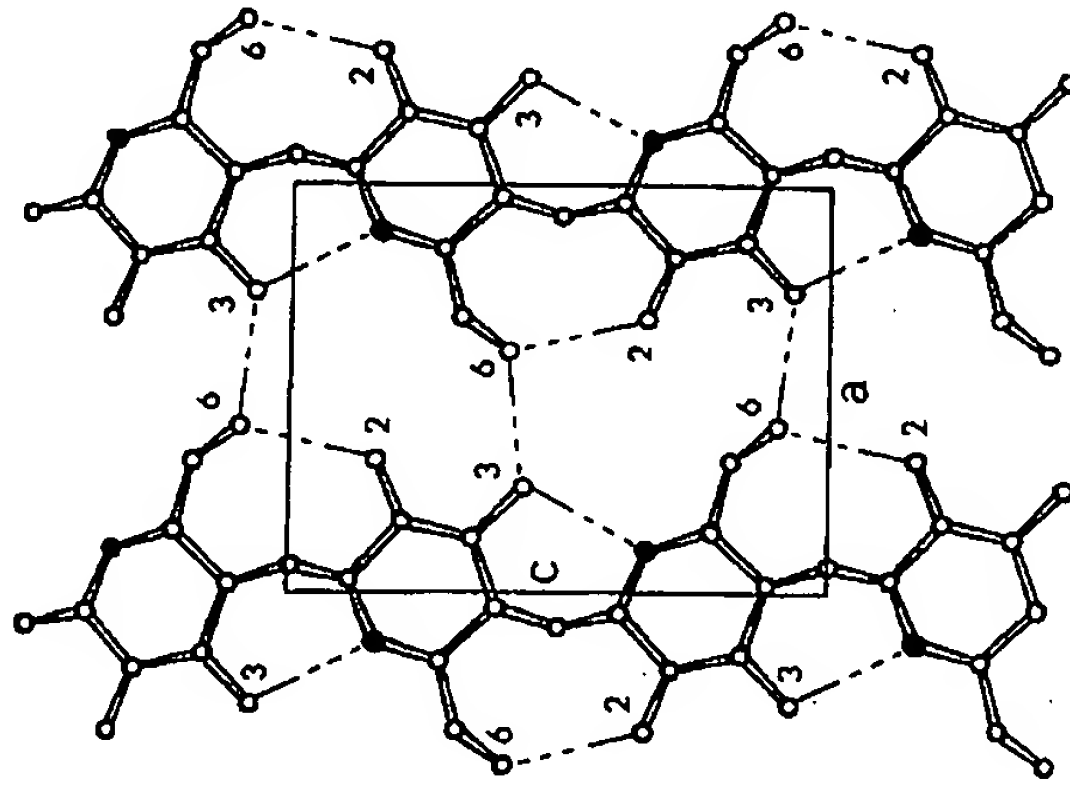


Fig. 3-8. Projection of the (O2O) plane in cellulose I, showing the hydrogen bonding network and the numbering of the atoms. Each glucose residue forms two intramolecular hydrogen bonds (O3-H...O5' and O6...H-O2') and one intermolecular bond (O6-H...O3). (Slightly modified from Gardner and Blackwell, 1974.)

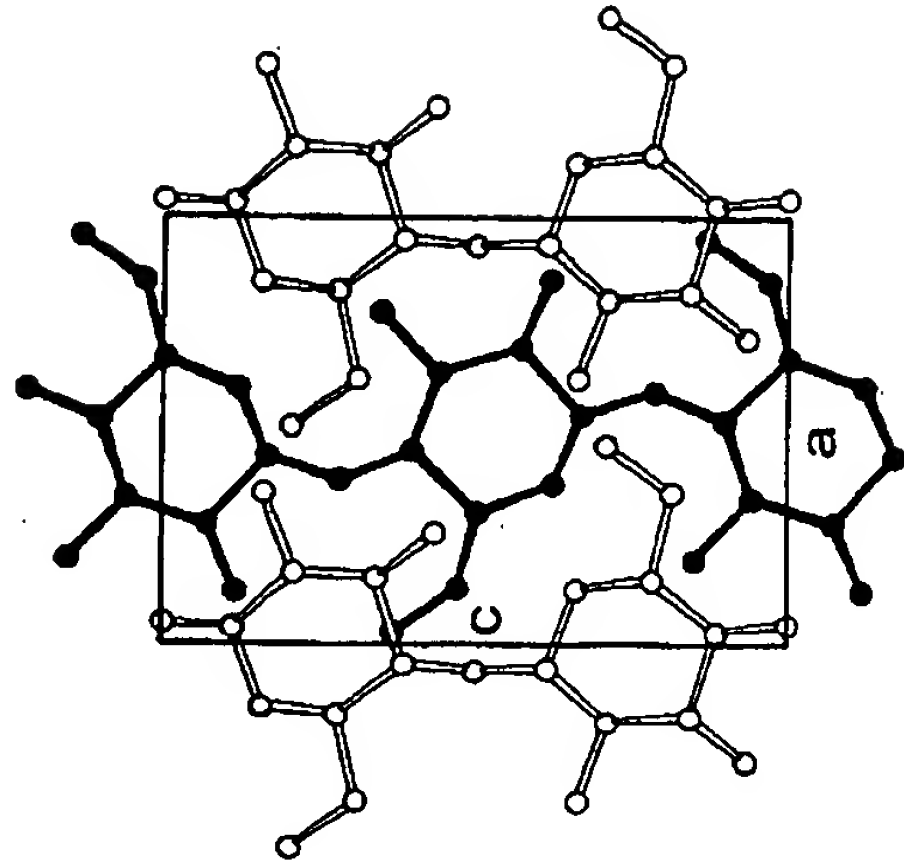


Fig. 3-9. Projection of the chains in cellulose II perpendicular to the *ac* plane. The center chain (black) is staggered and antiparallel to the corner chains. (Reproduced from Kolpak et al., 1978, *Polymer* 19, 123-131, by permission of the publishers, IPC Business Press Ltd. ©.)

a-c plane are the same as in cellulose I. In addition, there are two hydrogen bonds between a corner chain and a center chain (Fig. 3-6), namely from O(2) in one chain to O(2)H in the other and also from O(3)H to O(6). Cellulose II is formed whenever the lattice of cellulose I is destroyed, for example on swelling with strong alkali or on dissolution of cellulose. Since the strongly hydrogen bonded cellulose II is thermodynamically more stable than cellulose I, it cannot be reconverted into the latter. All naturally occurring cellulose has the structure of cellulose I. Celluloses III and IV are produced when celluloses I and II are subjected to certain chemical treatments and heating.

The proportions of ordered and disordered regions of cellulose vary considerably depending on the origin of the sample (cf. Table 9-1). Cotton cellulose is more crystalline than cellulose in wood.

3.2.2 The Chain Length and Polydispersity of Cellulose

The polymer properties of cellulose are usually studied in solution, using solvents, such as CED or Cadoxen (see Section 9.2). On the basis of the solution properties, conclusions can be drawn concerning the average molecular weight, polydispersity, and chain configuration. However, the